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**Determination of Particle-associated PAH Derivatives (C1PAHs, NPAHs, OPAHs)  
in Ambient Air and Automobile Exhaust by Gas Chromatography/Mass  
Spectrometry with Negative Chemical Ionization**

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**ABSTRACT**

The concentrations of functionalized polycyclic aromatic hydrocarbons (PAHs),  
i.e., oxygenated PAHs (OPAHs), nitrated PAHs (NPAHs), and chlorinated PAHs  
(C1PAHs), in soluble organic fractions of automobile exhaust particles (NIST SRM  
1975 and NIES CRM No.8) and airborne particles (NIST SRM1648a and PM<sub>2.5</sub>  
collected at Kyoto, Japan) were simultaneously determined using gas  
chromatography–mass spectrometry with negative chemical ionization (GC–NCI–MS).  
The concentrations of PAH derivatives in standard reference materials determined by  
GC–NCI–MS were in good agreement with the certified and literature values. Ten  
OPAHs, 12 NPAHs, and 12 C1PAHs were detected in ambient PM<sub>2.5</sub> collected in Kyoto,

26 Japan by the proposed analytical method.

27

## 28 INTRODUCTION

29 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hazardous  
30 compounds because of their mutagenic and carcinogenic properties (1). PAHs are  
31 primarily produced as incomplete combustion products from organic materials such as  
32 wood, fossil fuels, and other organic substances (2–4). As a result, PAHs are detected in  
33 a variety of environmental media including air, soil, sediments, and organisms (5–8).  
34 Oxygenated PAHs (OPAHs), nitrated PAHs (NPAHs), and chlorinated PAHs (CIPAHs)  
35 make up of a class of PAH derivatives that pose a threat to human health because of  
36 their toxicity (9–12). These compounds are present in ambient air particles emitted by  
37 combustion processes or formed in the atmosphere via gaseous or heterogeneous  
38 reactions (13–15).

39 PAH derivatives are usually quantified by liquid chromatography equipped  
40 with mass spectrometry (LC–MS), liquid chromatography equipped with tandem mass  
41 spectrometry (LC–MS–MS), and gas chromatography–mass spectrometry (GC–MS)  
42 (16–20). Other analytical techniques such as high-performance LC (HPLC) with  
43 chemiluminescence detection, HPLC with fluorescence detection, two-dimensional GC  
44 time-of-flight mass spectrometry (GC × GC–ToFMS), and ultra-high-performance  
45 liquid chromatography with ToFMS have also been employed (21–25). In the GC–MS  
46 using negative chemical ionization (GC–NCI–MS) mode, highly electronegative  
47 compounds such as NPAH and CIPAHs are easily ionized by resonance capture of  
48 thermal electrons. Accordingly, GC–NCI–MS has also been widely used to determine  
49 PAH derivatives (OPAHs, NPAHs, and CIPAHs) because of its high sensitivity and  
50 selectivity (26–30); however, the simultaneous analysis of OPAHs, NPAHs, and

CIPAHs using GC–NCI–MS has not been reported yet.

In general, standard reference materials (SRM) issued by the National Institute of Standards and Technology (NIST; MD, USA) have been used to evaluate analytical methods for determining select chemical compounds. SRM 1975 (diesel particle extract) is an extract of SRM 2975 (diesel particle matter) in dichloromethane. The concentrations of 19 NPAHs in SRM1975 have been reported (31). Although the concentration of individual OPAHs in SRM1975 was reported by several researchers (16, 17, 20, 24), it has not been certified by NIST. Only one paper reported the concentration of CIPAHs in SRM 1975 using GC × GC–ToFMS (24). In the present study, we modified and simplified a GC–NCI–MS method to simultaneously determine 28 OPAHs, 37 NPAHs, and 16 CIPAHs and applied the method to their quantification in SRMs and ambient particulate matter samples.

## MATERIAL AND METHODS

### Chemicals and reagents

The target compounds in this study were 28 OPAHs, 37 NPAHs, and 16 CIPAHs. The abbreviations used for the individual OPAHs, NPAHs, and CIPAHs are shown in Table S1. The analytical standards of OPAHs and NPAHs were purchased from a variety of commercial suppliers. With the exceptions of 2-chloroanthracene (2-ClAnt) and 9-chloroanthracene (9-ClAnt), which were purchased from Sigma-Aldrich (MO, USA), the analytical standards of CIPAHs were synthesized by the authors. The detailed synthetic procedures for these CIPAHs have been reported in previous studies (30, 32, 33). The following deuterated compounds were used as internal standards: 9-fluorenone-*d*<sub>8</sub> (9-FluO-*d*<sub>8</sub>), 9,10-anthraquinone-*d*<sub>8</sub> (9,10-AntQ-*d*<sub>8</sub>), 1-nitropyrene-*d*<sub>9</sub> (1-NPyr-*d*<sub>9</sub>), and 6-nitrobenzo[*a*]pyrene (6-NBaP-*d*<sub>11</sub>). 9-FluO-*d*<sub>8</sub> was



purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and the remaining compounds were purchased from C/D/N Isotopes Inc. (Quebec, Canada). The solvents used for extraction and cleanup were pesticide analysis grade and were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) or Kanto Chemical Co., Inc. (Tokyo, Japan).

## Sample information

Two standard reference materials (SRM 1648a—urban particulate matter—and SRM 1975—diesel particulate extract) were selected and analyzed to validate the accuracy and precision of the method used in this study. These reference materials were purchased from NIST and stored according to recommendations (31, 34).

The vehicle exhaust particulate sample (CRM No.8) was purchased from the National Institute for Environmental Studies (NIES; Tsukuba, Japan). CRM No.8 was collected from electrostatic precipitators in huge ventilators connected to a highway tunnel (35, 36).

Ambient PM was sampled in the city of Kyoto (latitude 35°1'26''N, longitude 135°46'37''E), which is located ~100 m from the nearest busy road. PM samples were collected on 20.3 × 25.4 cm quartz fiber filters (QFF; QR-100, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) using a high-volume air sampler equipped with a PM<sub>2.5</sub> impactor (HV-1000F; SIBATA Scientific Technology Ltd., Saitama, Japan) operating at a constant flow rate of 0.7 m<sup>3</sup> min<sup>-1</sup>. Sampling was carried out over a 24 h period on November 29, 2014. After sampling, each QFF was cut into quarters, wrapped in aluminum foil, sealed, and stored in a freezer at -30°C until extraction for the analysis of PAH derivatives.

## Sample extraction and cleanup for GC analysis

The PAH derivatives in six ~200 mg subsamples of particulate samples (SRM 1648a and CRM No.8) were extracted using a Soxhlet extractor for 18 h with 300 mL of dichloromethane (DCM) containing 9-FluO-*d*<sub>8</sub>, 9,10-AntQ-*d*<sub>8</sub>, 1-NPyr-*d*<sub>9</sub>, and 6-NBaP-*d*<sub>11</sub> as internal standards. The extracts of particulate samples were concentrated to ca. 2 mL using a rotary evaporator and a gentle stream of nitrogen gas at 40°C. After the addition of 50 mL of *n*-hexane to the extracts, the solutions were concentrated to ca. 100 µL. Four subsamples of QFFs were then ultra-sonicated with 200 mL of DCM containing internal standards. The sample extracts were concentrated by the same method used for the samples for Soxhlet extraction. Six subsamples containing 100 µL of SRM 1975 were solvent-changed to *n*-hexane. The concentrated solutions were cleaned up using a silica-gel column (1g/6 mL, GL Science Inc., Tokyo, Japan). The silica-gel column was prewashed with 20 mL of *n*-hexane, and the target compounds were eluted with 50 mL of 40% DCM in *n*-hexane. The eluted solution was concentrated to ca. 50 µL by rotary evaporation under a gentle stream of nitrogen gas at 40°C. Fluor-*d* was added to the solution as an internal standard. The sample solutions were stored in a freezer at –20°C until GC-MS analysis. During all sample treatments, the samples were protected from light to avoid photochemical degradation of the analytes by using amber glassware or wrapping the glassware with aluminum foil.

## GC-MS analysis

In this study, we sought to simultaneously analyze 28 OPAHs, 37 NPAHs, and 16 CIPAHs using GC–NCI–MS, which shows high sensitivity and selectivity for PAH derivatives, as mentioned in the introduction. The chemical analysis of all samples was performed using a GCMS-QP2010 Plus (Shimadzu Corp., Kyoto, Japan) with a ZB-5ms

GC capillary column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness; Phenomenex Inc., CA, USA). Ultra-pure helium (99.9999%) was used as the carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>. During analysis, then oven temperature was maintained at 100°C for 4 min, increased from 100°C to 240°C at a rate of 20°C min<sup>-1</sup>, increased from 240°C to 310°C at a rate of 5°C min<sup>-1</sup>, and then kept at 310°C for 15 min, resulting in a total runtime of 40.0 min. The temperatures of the injector and GC-MS transfer line were maintained at 260°C and 280°C, respectively. The injection mode was pulsed splitless mode fitted with a glass liner and wool. The pulse pressure was 300 kPa for 3.0 min, and the sample injection volume was 1.0  $\mu$ L. The MS system was run in NCI mode, and the ionization energy was 70 eV. Methane (99.9999%) was used as the reagent gas at a flow rate of 0.31 mL min<sup>-1</sup>. The MS instrument was operated in selected ion monitoring (SIM) mode. The ionization current was kept at 60  $\mu$ A.

### Method calibration and validation

The calibration curve ranged from 0.6 to 300 ng mL<sup>-1</sup> and included eight calibration points. The detection limit (DL) of the target PAH derivatives was estimated as three times the standard deviation from repeated ( $n = 10$ ) analyses of a diluted standard solution. The calibration standard of the lowest concentration was repeatedly analyzed, and a standard deviation was calculated for each compound. To evaluate the applicability of the present method for determining particle-bound PAH derivatives, recovery experiments were conducted using the QFF sample and CRM No. 8. A sheet of QFF was cut into quarters after the sample collection, and 100 ng of standard PAH derivatives were spiked on three of them. The standard-spiked samples and a non-spiked sample were analyzed in accordance with the method described above. The recovery percentage of the PAH derivatives from QFF were calculated based on the

analytical results of the spiked and non-spiked QFF samples. The recoveries of the PAH derivatives from CRM No.8 were also tested by a similar manner, i.e., 100 ng of each PAH derivative was added to 200 mg of the CRM and analyzed as described above. Procedural blanks were also analyzed to monitor for contamination or interference. None of the targeted PAH derivatives were detected in the procedural blank samples. To verify the stability of the instrument, calibration standards for PAH derivatives were analyzed after every five samples.

### Standard addition to extracts of diesel particles and ambient air particles

To evaluate the matrix effects of the analytical method used to determine PAH derivatives in this study, we quantified SRM 1975 using both internal standard and standard addition quantitation methods. Standard addition samples consisted of four dilutions. In each dilution, 50  $\mu\text{L}$  of extract was placed into a 300- $\mu\text{L}$  chromatography vial after cleanup using an SPE silica-gel column. For the initial dilution, an additional 100  $\mu\text{L}$  of isooctane was added to make a total volume of 200  $\mu\text{L}$ . In each subsequent addition, 50  $\mu\text{L}$  of target PAH derivatives stock solutions (50, 75, or 150  $\text{ng mL}^{-1}$ ) were added.

## RESULTS AND DISCUSSION

Figure S1 shows a typical chromatogram of the target compounds. The peak numbers, retention times, monitored ions, coefficient of determination ( $r^2$ ) of the calibration curves, LODs, and analytical recoveries (%) are listed in Table S1. The  $r^2$  values, which were determined based on eight-point calibration curves, ranged from 0.9457 (6,12-benzo[*a*]pyrenequinone; 6,12-BaPQ) to 0.9997 (9-fluorenone; 9-FluO) for OPAHs. For NPAHs,  $r^2$  ranged from 0.9578 (5-nitroacenaphthene; 5-NAce) to 0.9991

(9-nitroanthracene; 9-NAnt) with good linearity. The  $r^2$  values of ClPAHs also showed good linearity with  $0.9674$  (7-chlorobenz[*a*]anthracene; 7-ClBaA)  $< r^2 < 0.9998$  (3,8-dichlorofluoranthene; 3,8-Cl<sub>2</sub>Fluor). Using the calibration curves described above, the LODs were determined as the lowest concentration of each target compound than could be determined (estimated as three times of the standard deviation from 10 repeated analyses of the calibration standard of the lowest concentration). The LODs ranged from 0.10 pg (9-FluO) to 95.64 pg (5,12-NaphthQ) for OPAHs, 0.10 pg (9-NAnt) to 29.50 pg (3-nitroperylene; 3-NPery) for NPAHs, and 0.08 pg (3,8-Cl<sub>2</sub>Fluor) to 7.54 pg (9-ClAnt) for ClPAHs (Table S1). The analytical recoveries of the targeted OPAHs in the QFFs and CRM No.8 ( $n = 3$ ) ranged from 70.2% (7,10-benzo[*a*]pyrenequinone, 7,10-BaPQ) to 108.4% (2-methylanthraquinone, 2-MeAntQ) and from 70.1% (1,2-naphthoquinone, 1,2-NapQ) to 113.0% (benzanthrone, BAntO), respectively. For NPAHs, analytical recoveries in QFFs and CRM No.8 ranged from 68.2% (5-nitroquinoline, 5-NQL) to 121.8% (1-nitroperylene, 1-NPery) and from 70.5% (2-nitrobiphenyl, 2-NBP) to 118.2% (3-NPery), respectively. In addition, those of ClPAHs in the QFFs and CRM No.8 ranged from 74.0% (9-chloroanthracene, 9-ClAnt) to 110.2% (1,3-dichlorofluoranthene, 1,3-Cl<sub>2</sub>Fluor) and from 88.0% (9-ClAnt) to 112.2% (dichlorobenzo[*a*]pyrene, Cl<sub>2</sub>BaP), respectively. Furthermore, the recoveries of the internal standard spiked into individual samples were 91.2% for FluO-*d*<sub>8</sub>, 95.4% for 9,10-AntQ-*d*<sub>8</sub>, 92.8% for 1-NPyr-*d*<sub>9</sub>, and 87.4% for 6-NBaP-*d*<sub>11</sub>. These results indicate that the analytical method was appropriate for analyzing PAH derivatives.

#### PAH derivatives in SRM and CRM samples

Two NIST standard reference samples containing PAH derivatives (SRM 1975, diesel particulate extract and SRM 1648a, urban particulate matter) and one NIES

reference material (CRM No.8, vehicle exhaust particulates) were analyzed to evaluate the GC-NCI-MS method for simultaneous qualitative and quantitative analysis proposed in this study. Target compounds were identified on the basis of comparison of retention time and accurate MS masses obtained from analytical standard. Results of PAHs derivative concentrations are shown in Figure 1, and summarized in Table 1. Several OPAHs were observed at high levels in all samples. The concentrations of individual OPAHs observed in the three samples were on the same order of magnitude, with the exceptions of 9-FluO and 9,10-phenanthrenequinone (9,10-PheQ). The concentrations of 9-FluO in SRM 1975 and CRM No. 8 were approximately 7.5- and 30-times higher than those in SRM 1648a, respectively, while those of 9,10-PheQ were 20- and 25-times higher, respectively. The NPAHs concentrations determined in the three samples were on the same order of magnitude, with the exception of 1-NPyr in SRM 1975. Tables 2 and 3 compare the OPAH and NPAH concentrations in SRM 1975 with those reported by NIST and in previous works (16, 17, 20, 24, 28, 29, 32, 33).

#### **OPAHs concentrations in SRM and CRM samples**

For OPAHs, the determined concentrations were generally in good agreement with the literature values for SRM 1975. However, the concentration of 1,2-naphthoquinone (1,2-NapQ) was 100-times lower than the literature value obtained by GC-ToFMS. The concentrations of 9-FluO, 9,10-anthraquinone (9,10-AntQ), 2-MeAntQ, benzo[*a*]fluorenone (BaFluO), 5,12-naphthacenequinone (5,12-NaphQ), and 7,12-benz[*a*]anthracenequinone (7,12-BaAQ) in SRM 1975 have been reported in several works, although 5,12-NaphQ was not detected by our method. This might be due to the high LOD (Table S1, 95.64 pg) of 5,12-NaphQ observed in this study. The determined concentrations of 9-FluO, 9,10-AntQ, 2-MeAntQ, and BaFluO in SRM

1975 fell within the 95% confidence interval for the literature values; however, the concentration of 7,12-BaAQ ( $15.2 \pm 3.11$ ) observed in SRM 1975 was beyond the range of previously reported values ( $0.79 \pm 0.03$  to  $12.1 \pm 1.29$ ). In addition, compared to previous reports, high concentrations of 9,10-PheQ and 6H-benzo[*cd*]pyren-6-one (BcdPyO) were observed in this study. The discrepancy in the quantitative values between previous studies and the present study may be attributed to matrix effects. To evaluate the matrix effects in the method used to determine PAH derivatives in this study, all PAH derivatives in SRM 1975 were analyzed using both internal standard and standard addition quantitation methods. All PAH derivatives that were identified using internal standard quantitation were successfully identified in the series of standard additions. The quantitative concentrations of NPAHs and ClPAHs determined using the two quantitation methods were in good agreement (differences of less than 15%). However, the concentrations of some OPAHs obtained by the two methods were not consistent. Figure 2 shows the concentrations of OPAHs in SRM 1975 measured using both methods. The concentrations of 12 OPAHs identified in SRM 1975 using the internal standard method were in less than 25% difference with those determined using the standard addition method: 1,2-NapQ (5% difference), 1,4-NapQ (11%), 9-FluO (6%), XaO (11%), AceQ (9%), 9,10-AntQ (4%), 2-MeAntQ (8%), 2-N-9-FluO (25%), BaFluO (8%), BAntO (8%), AceAntQ (22%), 4,5-PyrQ (22%), 7,12-BaAQ (15%), BcdPyO (14%), 3-NBAntO (10%), and 6,12-BaPQ (2%); however, significant differences with  $p < 0.05$  (Student's *t*-test) between the two methods were found for 9,10-PheQ (71%) and 5,6-ChryQ (101%). These differences may be attributed to matrix effects, which enhanced the response of the quantified ion in the internal standard method compared to that in the standard addition method. Similar matrix enhancement has been reported previously (16). The apparent enhancement in response may have

been due to contamination in the GC-MS instrument or from interference by a component of the diesel extract. Overall, the results obtained using the internal standard and standard addition methods in this study were in good agreement, with the concentrations of all PAH derivatives differing by less than 25%, except for 9,10-PheQ and 5,6-ChryQ. This suggests that the concentrations of 9,10-PheQ and 5,6-ChryQ obtained in this study were overestimated due to matrix effects. Thus, when matrix-interfering ingredients differ from sample to sample, the standard addition method is not usually employed for quantitation. In the present study, the internal standard method seemed reasonable for the quantitation of PAH derivatives, with the exceptions of 9,10-PheQ and 5,6-ChryQ. To correct the quantified values of 9,10-PheQ and 5,6-ChryQ, other labeled OPAH standards should be carefully considered.

Selected OPAH concentrations in CRM No.8 and SRM 1648a are summarized in Table 4. Of the 12 OPAHs detected in CRM No.8 in this study, five were observed at similar concentration levels in a previous study (25). The OPAH concentrations determined in SRM 1648a in this study were similar to those reported in previous studies (20, 25). In particular, the concentration of 7,12-BaAQ determined in this study was in good agreement with the results obtained by Nocun and Schantz (20).

### **NPAHs concentrations in SRM and CRM samples**

The concentrations of the target NPAHs detected in SRM 1975 in this study are compared with the NIST certified and reference values in Table 3. The concentrations of 9-NAnt and 1-NPyr in SRM 1975 determined in this study were in good agreement with the NIST certified values. In contrast, the concentration of 6-NChry was approximately 10% higher than the NIST certified value. The other NPAHs measured in SRM 1975 in this study fell within the 95% confidence interval for the reference and literature values.



Selected NPAH concentrations determined in CRM No.8 and SRM 1648a are summarized in Table 4. Of the eight NPAHs detected in CRM No.8 in this study, only that of 9-NAnt was detected in the previously report (25). The concentrations of NPAHs detected in SRM 1648a were in good agreement with the NIST reference values, except for 2-NNap, 3-NBP, and 5-NAce. Significant differences in the concentrations compared to the NIST reference values were found for those compounds.

### CIPAHs concentrations in SRM and CRM samples

Of the 16 target CIPAHs, five were detected SRM 1975. Among the observed CIPAHs, 2-ClAnt and 9-ClAnt were detected in relatively high contents, representing a total of 77% of the total CIPAH concentration. The next most abundant CIPAH was 1-ClPyr (16%). A similar CIPAH composition was observed in SRM 1975 in a previous report that used two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (24). In addition, six CIPAHs were detected in CRM No.8; 2-ClAnt was the major component (~40% of total CIPAHs) followed by 1-ClPyr (27%) and 9-ClAnt (17%). Similar high contributions of 2-ClAnt, 9-ClAnt, and 1-ClPyr were observed in tunnel dust in Japan (18). The observed CIPAH concentration, particularly the significant contributions of CIPAHs with three and four rings, might be a characteristic indicator of vehicle exhaust. On the other hand, eight CIPAHs were detected in SRM 1648a; 1-ClPyr was the dominant contributor (~35% of total CIPAHs,  $0.05 \pm 0.002$  mg  $\text{kg}^{-1}$ ) followed by 6-ClBaP (20%,  $0.03 \pm 0.001$  mg  $\text{kg}^{-1}$ ; Table 1). 6-ClBaP accounted for only 2% of total CIPAHs in CRM No.8. In this aspect, the distribution of CIPAHs in vehicle exhaust particulate differed significantly from that in urban air particles.

### PAHs derivatives in ambient particle

The concentrations of PAH derivatives measured in the PM<sub>2.5</sub> sample are summarized in Table 1. Of the 28 target OPAHs, 10 were detected in the ambient air particle samples. The most abundant OPAH was 7,12-BaAQ ( $100.5 \pm 15.21 \text{ pg m}^{-3}$ ) followed by BAntO ( $48.4 \pm 4.87 \text{ pg m}^{-3}$ ) and BaFluO ( $39.8 \pm 5.21 \text{ pg m}^{-3}$ ). Similar 7,12-BaAQ concentrations were measured in ambient air samples in Osaka, Japan (38, 39). The concentrations of 9-FluO, 9,10-AntQ, and BAntO observed in this study were of a similar magnitude compared to those determined in air in Tokyo, Japan (40). The total concentration of OPAH in this study was  $315.1 \pm 38.1 \text{ pg m}^{-3}$ , while the total concentrations of NPAHs and CIPAHs were approximately one order of magnitude higher.

Of the 37 target NPAHs, 13 NPAHs were detected in this study. The three most abundant NPAHs in the ambient particle sample were 9-NAnt, 2-/3-NFluor, and 1-NPyr (50.3%, 28.6%, and 5.3% of the total NPAH concentration, respectively). The concentrations of NPAHs were similar to those determined in Tokyo, Japan (40), Chiang Mai, Thailand (41), and Hanoi, Vietnam (42).

Twelve species of CIPAHs were detected in the ambient particle sample. Among the detected CIPAHs, the most abundant was 6-ClBaP ( $7.16 \pm 0.87 \text{ pg m}^{-3}$ ) followed by 1-ClPyr ( $4.52 \pm 0.51 \text{ pg m}^{-3}$ ) and 7-ClBaA ( $2.12 \pm 0.24 \text{ pg m}^{-3}$ ). Similar concentrations were observed in Nagoya, Japan (30) and Shizuoka, Japan (18, 32, 43). In addition, the CIPAH composition was similar to that observed in SRM 1648a but not to the compositions found in SRM 1975 and CRM No.8.

## CONCLUSION

This study reports the simultaneous determination for PAH derivatives (OPAHs, NPAHs, and CIPAHs) in automobile exhaust particles and airborne particles using

GC–NCI–MS. The proposed GC–NCI–MS method enables the separation and analysis of 84 PAH derivatives with an analysis time of 40 min and yields good recovery values. The standard addition method indicated the potential enhancement of 9,10-PheQ and 5,6-ChryQ. Further consideration is needed for the quantification of those compounds using an internal standard method. Currently, very few labeled OPAHs are commercially available; thus, this work highlights the need for improved internal standards for a few OPAHs. On the other hand, the concentrations of all PAH derivatives determined by the internal standard and standard addition quantitation methods didn't shows significant difference, except for 9,10-PheQ and 5,6-ChryQ. In addition, the concentrations of PAH derivatives in several standard reference materials and airborne particles collected in Kyoto were quantified using GC–NCI–MS with the internal standard method, and the results showed good agreement with the literature values. As far as we know, this is the first report of multicomponent simultaneous determination of 84 PAH derivatives, including 28 OPAHs, 37 NPAHs, and 16 CIPAHs, using single GC–NCI–MS. Hence, we expect that the separation and quantitation method provided in this work will improve the sensitivity of the GC–NCI–MS quantitation of PAH derivatives in the future studies. These results indicate that vehicle exhaust might be a minor contributor to particulate CIPAHs in the air, while other emission sources are likely the major contributors in the study sites.

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503 Table 1 Simultaneous GC–NCI–MS determination of PAH derivatives in SRM 1975,  
504 CRM No.8, SRM 1648a, and PM<sub>2.5</sub> in Kyoto, Japan.

Target compound	SRM1975, <i>n</i> =6		CRM No.8, <i>n</i> =6		SRM 1648a, <i>n</i> =6		PM <sub>2.5</sub> in Kyoto, <i>n</i> =4	
	<sup>a</sup> mg kg <sup>-1</sup>	<sup>b</sup> SD	mg kg <sup>-1</sup>	SD	mg kg <sup>-1</sup>	SD	pg m <sup>-3</sup>	SD
<i>OPAHs</i>								
1,2-NapQ	0.23	0.02	0.46	0.02	0.06	0.001	0.80	0.02
1,4-NapQ	0.02	0.002	<DL		0.65	0.03	<DL	
1-AceO	<sup>c</sup> <DL		<DL		0.06	0.001	0.70	0.05
9-FluO	6.16	0.84	25.0	3.21	0.81	0.02	24.0	4.10
XaO	1.56	0.21	3.11	0.54	<DL		<DL	
AceQ	7.61	0.95	15.2	2.66	0.02	0.001	<DL	
9,10-AntQ	7.07	1.01	16.3	3.14	2.52	0.21	38.2	5.14
1,4-AntQ	<DL		<DL		<DL		<DL	
2-MeAntQ	3.12	0.50	6.24	1.21	1.25	0.08	10.2	2.14
9,10-PheQ	12.7	2.11	19.4	5.52	0.60	0.002	17.5	4.21
2-N-9-FluO	0.1	0.01	<DL		<DL		<DL	
BaFluO	4.32	0.85	1.96	0.16	3.01	0.54	39.8	5.21
BAntO	10.7	1.54	3.51	0.71	4.53	0.65	48.4	4.87
AceAntQ	1.21	0.14	2.43	0.32	<DL		<DL	
4,5-PyrQ	12.4	1.65	<DL		<DL		<DL	
1,6-PyrQ	<DL		<DL		<DL		<DL	
7,12-BaAQ	15.2	2.31	3.4	0.21	5.16	0.98	100.5	15.21
1,8-PyrQ	<DL		<DL		<DL		<DL	
1,4-ChryQ	<DL		<DL		<DL		<DL	
2,7-DN-9-FluO	<DL		<DL		<DL		<DL	
5,12-NaphthQ	<DL		<DL		<DL		<DL	
5,6-ChryQ	6.95	0.68	<DL		<DL		<DL	
BcdPyO	11.5	1.36	8.2	0.85	4.57	0.21	35.0	3.25
3-NBAntO	1.15	0.20	<DL		<DL		<DL	
7,10-BaPQ	<DL		<DL		<DL		<DL	
6,12-BaPQ	1.03	0.08	<DL		<DL		<DL	
1,6-BaPQ	<DL		<DL		<DL		<DL	
6,13-PentQ	<DL		<DL		<DL		<DL	
Total OPAHs	103.0	18.2	105.2	14.8	23.2	2.54	315.1	28.1
<i>NPAHs</i>								
5-NQL	0.02	0.001	<DL		<DL		<DL	
1-NNap	0.04	0.004	0.08	0.001	0.01	0.001	0.72	0.07
2-Me-1-NNap	0.02	0.003	0.03	0.001	<DL		<DL	
2-NNap	0.08	0.003	0.08	0.002	0.01	0.001	<DL	
2-NBP	<DL		<DL		<DL		<DL	
3-NBP	0.06	0.01	0.05	0.001	0.01	0.001	0.59	0.15
1,5-DNNap	<DL		<DL		<DL		<DL	
1,3-DNNap	<DL		<DL		<DL		<DL	
5-NAce	0.09	0.01	0.06	0.002	0.01	0.002	0.93	0.34
2,7-DNNap	<DL		<DL		0.003	0.0003	<DL	
2-F-7-NFlu	<DL		<DL		<DL		<DL	
2-NFlu	0.15	0.01	<DL		<DL		<DL	
9-NAnt	1.30	0.21	1.54	0.57	0.18	0.01	25.31	4.68
1,8-DNNap	0.34	0.02	<DL		<DL		<DL	
9-NPhe	0.25	0.01	0.45	0.001	0.003	0.0001	0.39	0.04
3-NPhe	0.21	0.01	0.39	0.002	0.04	0.001	2.42	0.54
2-NAnt	<DL		<DL		<DL		<DL	
9,10-DNAnt	<DL		<DL		<DL		<DL	
2-/3-NFluor	1.85	0.15	<DL		0.27	0.01	14.4	1.95
4-NPyr	0.07	0.01	<DL		0.01	0.001	0.20	0.01
1-NPyr	17.1	1.64	<DL		0.12	0.002	2.70	0.24
2-NPyr	<DL		<DL		0.08	0.001	0.57	0.01
7-NBaA	2.02	0.21	<DL		0.06	0.001	0.94	0.31
1-NTP	0.46	0.01	<DL		<DL		<DL	
6-NChry	0.95	0.15	<DL		0.01	0.001	0.19	0.04
2-NTP	<DL		<DL		<DL		<DL	

1,3-DNPyr	0.70	0.03	<DL		<DL		<DL	
1,6-DNPyr	1.42	0.15	<DL		<DL		<DL	
1,8-DNPyr	1.71	0.36	<DL		<DL		<DL	
1-NPery	0.91	0.09	<DL		<DL		<DL	
6-NBaP	0.38	0.06	<DL		0.05	0.002	0.94	0.04
3-NBkF	0.44	0.01	<DL		<DL		<DL	
3-NBeP	2.14	0.24	<DL		<DL		<DL	
1-NBaP	<DL		<DL		<DL		<DL	
3-NBaP	<DL		<DL		<DL		<DL	
3-NPery	<DL		<DL		<DL		<DL	
Total NPAHs	32.71	4.51	2.68	0.97	0.87	0.04	50.30	9.84
<i>CIPAHs</i>								
2-ClAnt	0.13	0.01	0.23	0.02	0.02	0.002	0.42	0.04
9-ClAnt	0.10	0.01	0.10	0.01	<DL		0.20	0.02
9,10-Cl2Ant	<DL		<DL		0.004	0.001	0.14	0.03
3-ClFluor	0.01	0.001	0.07	0.001	0.02	0.003	1.45	0.04
8-ClFluor	0.01	0.001	<DL		0.001	0.0001	0.15	0.01
1-ClPy	0.05	0.002	0.16	0.01	0.05	0.002	4.52	0.51
1,3-Cl2Fluor	<DL		<DL		<DL		0.003	0.0004
3,8-Cl2Fluor	<DL		<DL		<DL		0.001	0.0003
Cl2Py	<DL		<DL		0.01	0.001	0.53	0.01
3,4-Cl2Fluor	<DL		<DL		<DL		<DL	
7-ClBaA	<DL		0.02	0.001	0.01	0.002	2.12	0.24
Cl3Py	<DL		<DL		<DL		<DL	
Cl4Py	<DL		<DL		<DL		<DL	
6-ClBaP	<DL		0.01	0.002	0.03	0.001	7.16	0.87
Cl2BaP	<DL		<DL		<DL		0.84	0.04
Cl3BaP	<DL		<DL		<DL		<DL	
Total ClPAHs	0.30	0.02	0.59	0.05	0.15	0.01	17.5	1.74

<sup>a</sup>Mean concentration.

<sup>b</sup>Standard deviation.

<sup>c</sup><DL, below limit detection.

508 Table 2 OPAH concentrations (mg kg<sup>-1</sup>) in SRM 1975 (diesel particle extract).

	This study	O'Connell et al (16) <sup>a</sup>	Layshock et al. (17) <sup>b</sup>	Nocum and Schantz (21) <sup>c</sup>	Manzano et al. (25) <sup>d</sup>	Manzano et al. (25) <sup>e</sup>	Manzano et al. (25) <sup>f</sup>	Manzano et al. (25) <sup>g</sup>
1,2-NapQ	0.23 (0.02)	<sup>i</sup> NA	NA	NA	<DL	21.4 (8.56)	<DL	<DL
1,4-NapQ	0.02 (0.002)	<DL	NA	NA	<DL	0.44 (0.09)	<DL	<DL
9-FluO	6.16 (0.84)	2.6	2.69 (0.08)	7.37 (0.43)	11.4 (5.99)	9.64 (3.87)	203.7 (13.6)	5.15 (2.07)
XaO	1.56 (0.21)	<DL	NA	NA	NA	NA	NA	NA
AceQ	7.61 (1.45)	<DL	NA	NA	0.2 (0.01)	NA	<DL	22.8 (9.41)
9,10-AntQ	7.07 (1.01)	8.1	5.23 (0.16)	14.60 (1.57)	2.00 (0.30)	0.88 (0.10)	3.60 (1.71)	2.97 (0.34)
1,4-AntQ	<sup>h</sup> <DL	<DL	<DL	NA	<DL	1.27 (0.14)	<DL	0.36 (0.04)
2-MeAntQ	3.12 (0.50)	NA	NA	NA	3.39 (0.05)	2.65 (1.06)	2.17 (0.99)	1.8 (0.72)
9,10-PheQ	12.7 (3.11)	<DL	NA	NA	3.42 (0.32)	1.01 (0.40)	<DL	<DL
2-N-9-FluO	0.1 (0.01)	NA	NA	NA	NA	NA	NA	NA
BaFluO	4.32 (0.85)	1.8	3.43 (0.25)	7.74 (0.43)	7.73 (0.60)	4.3 (0.47)	5.64 (2.25)	5.33 (0.58)
BAntO	10.7 (2.54)	1.5	4.39 (0.34)	9.07 (0.56)	0.57 (0.20)	7.47 (0.81)	0.56 (0.24)	2.49 (0.27)
AceAntQ	1.21 (0.14)	<DL	NA	NA	<DL	9.55 (2.40)	<DL	<DL
4,5-PyrQ	12.4 (2.65)	<DL	NA	NA	NA	NA	NA	NA
7,12-BaAQ	15.2 (3.11)	3.40	0.79 (0.03)	12.66 (0.75)	12.1 (1.29)	9.73 (1.52)	6.35 (1.77)	3.58 (0.56)
5,12-NaphQ	<DL	<DL	7.22 (0.35)	0.90 (0.17)	<DL	<DL	0.68 (0.23)	0.64 (0.26)
5,6-ChryQ	6.95 (0.68)	NA	NA	NA	NA	NA	NA	NA
BcdPyO	11.5 (1.36)	0.71	1.87 (0.32)	15.00 (1.34)	<DL	<DL	<DL	<DL
3-NBAntO	1.15 (0.20)	NA	NA	NA	NA	NA	NA	NA
6,12-BaPQ	1.03 (0.08)	NA	NA	NA	NA	NA	NA	NA

<sup>a</sup>GC-EI-MS, DB-5MS.

<sup>b</sup>GC-EI-MS, DB-5MS.

<sup>c</sup>GC-EI-MS, DB-XLB.

<sup>d</sup>GC×GC/ToF-MS, Rtx-5MS×Rxi-17.

<sup>e</sup>GC×GC/ToF-MS, Rtx-5MS×Rxi-17 with no clean up.

<sup>f</sup>GC×GC/ToF-MS, LC-50×NSP-35.

<sup>g</sup>GC×GC/ToF-MS, LC-50×NSP-35 with no clean up.

<sup>h</sup><DL, below limit detection

<sup>i</sup>NA, not applicable

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514     Table 3 NPAH concentrations (mg kg<sup>-1</sup>) in SRM 1975 (diesel particle extract).

	This study	NIST	<sup>c</sup> Bezabeh et al. (28)	<sup>d</sup> Bezabeh et al. (28)	<sup>e</sup> Bamford et al. (29)	<sup>f</sup> Chiu and Miles (37)	<sup>g</sup> Manzano et al. (25)	<sup>g</sup> Manzano et al. (25)	<sup>h</sup> Manzano et al. (25)	<sup>i</sup> Manzano et al. (25)
5-NQL	0.02 (0.001)	<sup>k</sup> NA	NA	NA	NA	NA	NA	NA	NA	NA
1-NNap	0.04 (0.004)	<sup>a</sup> 0.01	NA	NA	0.01 (0.001)	NA	0.04 (0.01)	0.07 (0.01)	0.04 (0.00)	0.06 (0.006)
2-Me-1-NNap	0.02 (0.003)	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-NNap	0.08 (0.003)	<sup>a</sup> 0.04	NA	NA	0.04 (0.001)	NA	0.06 (0.01)	0.10 (0.01)	0.05 (0.01)	0.07 (0.01)
3-NBP	0.06 (0.01)	NA	NA	NA	<sup>l</sup> <DL	NA	<DL	<DL	0.05 (0.00)	0.04 (0.005)
5-NAce	0.09 (0.01)	NA	NA	NA	<DL	NA	<DL	<DL	<DL	<DL
2-NFlu	0.15 (0.01)	NA	NA	NA	<DL	NA	0.92 (0.04)	<DL	<DL	<DL
9-NAnt	1.30 (0.21)	<sup>b</sup> 1.24	1.36 (0.03)	1.28 (0.02)	1.28 (0.02)	1.19 (0.02)	1.56 (0.145)	1.56 (0.35)	1.56 (0.17)	1.39 (0.13)
1,8-DNNap	0.34 (0.02)	NA	NA	NA	NA	NA	NA	NA	NA	NA
9-NPhe	0.25 (0.01)	<sup>a</sup> 0.22	0.27 (0.001)	0.21 (0.005)	0.21 (0.005)	0.18 (0.063)	0.26 (0.02)	0.46 (0.04)	0.32 (0.05)	0.31 (0.03)
3-NPhe	0.21 (0.01)	<sup>a</sup> 0.08	NA	NA	0.08 (0.004)	NA	0.12 (0.05)	0.13 (0.01)	0.11 (0.01)	0.11 (0.01)
2-/3-NFluor	1.85 (0.15)	<sup>a</sup> 1.41	1.47 (0.01)	1.87 (0.024)	1.70 (0.02)	1.34 (0.034)	1.05 (0.07)	0.78	1.56	1.38
4-NPyr	0.07 (0.01)	<sup>a</sup> 0.07	NA	NA	0.07 (0.002)	NA	NA	NA	NA	NA
1-NPyr	17.1 (1.64)	<sup>b</sup> 16.6	16.4 (0.1)	16.1 (0.6)	16.07 (0.59)	16.6 (0.34)	18.8 (0.42)	20.7 (4.08)	18.0 (5.27)	16.0 (2.22)
7-NBaA	2.02 (0.21)	<sup>a</sup> 1.68	1.62 (0.03)	1.96 (0.07)	1.96 (0.07)	1.99 (0.12)	2.10 (0.28)	2.76 (0.20)	2.53 (0.88)	1.66 (0.12)
1-NTP	0.46 (0.01)	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-NChry	0.95 (0.15)	<sup>b</sup> 0.85	0.78 (0.01)	0.90 (0.015)	0.90 (0.002)	0.873 (0.13)	0.95 (0.16)	2.03 (0.76)	1.36 (0.73)	0.51 (0.10)
1,3-DNPyr	0.70 (0.03)	<sup>b</sup> 0.61	0.60 (0.01)	0.538 (0.039)	0.54 (0.04)	0.581 (0.093)	NA	NA	NA	NA
1,6-DNPyr	1.42 (0.15)	<sup>a</sup> 1.09	1.39 (0.04)	0.93 (0.014)	0.93 (0.01)	0.64 (0.112)	NA	NA	NA	NA
1,8-DNPyr	1.71 0.36)	<sup>a</sup> 1.29	1.55 (0.02)	1.38 (0.04)	1.38 (0.04)	0.495 (0.143)	NA	NA	NA	NA
1-NPery	0.91 (0.09)	NA	NA	NA	NA	NA	NA	NA	NA	NA

6-NBaP	0.38 (0.06)	<sup>a</sup> 0.49	0.64 (0.006)	0.51 (0.024)	0.51 (0.02)	0.456 (0.012)	NA	NA	NA	NA
3-NBkF	0.44 (0.01)	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-NBeP	2.14 (0.24)	<sup>a</sup> 2.01	2.2 (0.2)	1.83 (0.07)	1.83 (0.07)	<DL	NA	NA	NA	NA

<sup>a</sup>Reference concentration.

<sup>b</sup>Certified concentration.

<sup>c</sup>GC-NCI-MS, DB-5MS.

<sup>d</sup>GC-NCI-MS, DB-17MS.

<sup>e</sup>GC-NCI-MS.

<sup>f</sup>GC-HRMS, DB-5MS.

<sup>g</sup>GC×GC/ToF-MS, Rtx-5MS×Rxi-17.

<sup>h</sup>GC×GC/ToF-MS, Rtx-5MS×Rxi-17 with no clean up.

<sup>i</sup>GC×GC/ToF-MS, LC-50×NSP-35.

<sup>j</sup>GC×GC/ToF-MS,LC-50×NSP-35 with no clean up.

<sup>k</sup>NA, not applicable.

<sup>l</sup><DL, below limit detection.

517 Table 4 OPAH and NPAH concentrations (mg kg<sup>-1</sup>) in vehicle exhaust particulate and  
518 urban particulate matter.

	CRM No.8	CRM No.8	SRM 1648a	SRM 1648a	SRM 1648a	SRM 1648a
	This study	<sup>b</sup> Mirival et al. (26)	This study	NIST (32)	<sup>c</sup> Nocun and Schantz (25)	<sup>b</sup> Mirival et al. (26)
<i>OPAHs</i>						
1,2-NapQ	0.46 (0.02)	<sup>e</sup> NA	0.06 (0.001)	NA	NA	NA
1,4-NapQ	<sup>d</sup> <DL	NA	0.65 (0.03)	NA	NA	NA
1-AceO	<DL	NA	0.06 (0.001)	NA	NA	NA
9-FluO	25.0 (5.21)	NA	0.81 (0.02)	NA	1.12 (0.13)	NA
XaO	3.11 (0.54)	NA	<DL	NA	NA	NA
AceQ	15.2 (3.66)	NA	0.02 (0.001)	NA	NA	NA
9,10-AntQ	16.3 (4.14)	14.1 (0.85)	2.52 (0.21)	NA	4.57 (0.35)	3.16 (0.48)
2-MeAntQ	6.24 (1.21)	4.05 (0.45)	1.25 (0.08)	NA	NA	1.43 (0.18)
9,10-PheQ	19.4 (6.52)	11.4 (1.02)	0.60 (0.002)	NA	NA	0.52 (0.03)
BaFluO	1.96 (0.16)	1.50 (0.23)	3.01 (0.554)	NA	2.13 (0.45)	2.49 (0.33)
BAntO	3.51 (0.71)	1.89 (0.17)	4.53 (0.65)	NA	3.14 (0.22)	4.49 (0.66)
AceAntQ	2.43 (0.32)	NA	<DL	NA	NA	NA
7,12-BaAQ	3.4 (0.21)	<DL	5.16 (0.98)	NA	5.10 (0.41)	3.34 (0.35)
BcdPyO	8.2 (1.85)	NA	4.57 (0.21)	NA	NA	NA
<i>NPAHs</i>						
1-NNap	0.08 (0.001)	NA	0.01 (0.001)	<sup>a</sup> 0.009 (0.001)	NA	NA
2-Me-1-NNap	0.03 (0.001)	NA	<DL	NA	NA	NA
2-NNap	0.08 (0.002)	NA	0.01 (0.001)	<sup>a</sup> 0.007 (0.001)	NA	<DL
3-NBP	0.05 (0.001)	NA	0.01 (0.001)	<sup>a</sup> 0.004 (0.001)	NA	NA
5-NAce	0.06 (0.002)	<DL	0.01 (0.002)	<sup>a</sup> 0.004 (0.000)	NA	<DL
2,7-DNNap	<DL	NA	0.003 (0.0003)	NA	NA	NA
9-NAnt	1.54 (0.57)	0.95 (0.07)	0.18 (0.01)	<sup>a</sup> 0.18 (0.02)	NA	<DL
9-NPhe	0.45 (0.001)	NA	0.003 (0.0001)	<sup>a</sup> 0.003 (0.000)	NA	NA
3-NPhe	0.39 (0.002)	NA	0.04 (0.001)	NA	NA	NA
2-/3-NFluor	<DL	<DL	0.27 (0.01)	<sup>a</sup> 0.263 (0.03)	NA	<DL
4-NPyr	<DL	NA	0.01 (0.001)	<sup>a</sup> 0.008 (0.000)	NA	NA
1-NPyr	<DL	<DL	0.12 (0.002)	<sup>a</sup> 0.086 (0.007)	NA	0.16 (0.013)
2-NPyr	<DL	<DL	0.08 (0.001)	<sup>a</sup> 0.05 (0.002)	NA	<DL
7-NBaA	<DL	<DL	0.06 (0.001)	<sup>a</sup> 0.08 (0.001)	NA	<DL
6-NChry	<DL	NA	0.01 (0.001)	<sup>a</sup> 0.007 (0.000)	NA	<DL
6-NBaP	<DL	<DL	0.05 (0.002)	NA	NA	0.04 (0.0002)

<sup>a</sup>Reference value.

<sup>b</sup>HPLC-ToFMS.

<sup>c</sup>GC-EI-MS, DB-XLB.

<sup>d</sup><DL, below limit detection

<sup>e</sup>NA, not applicable

520 Figure captions

521

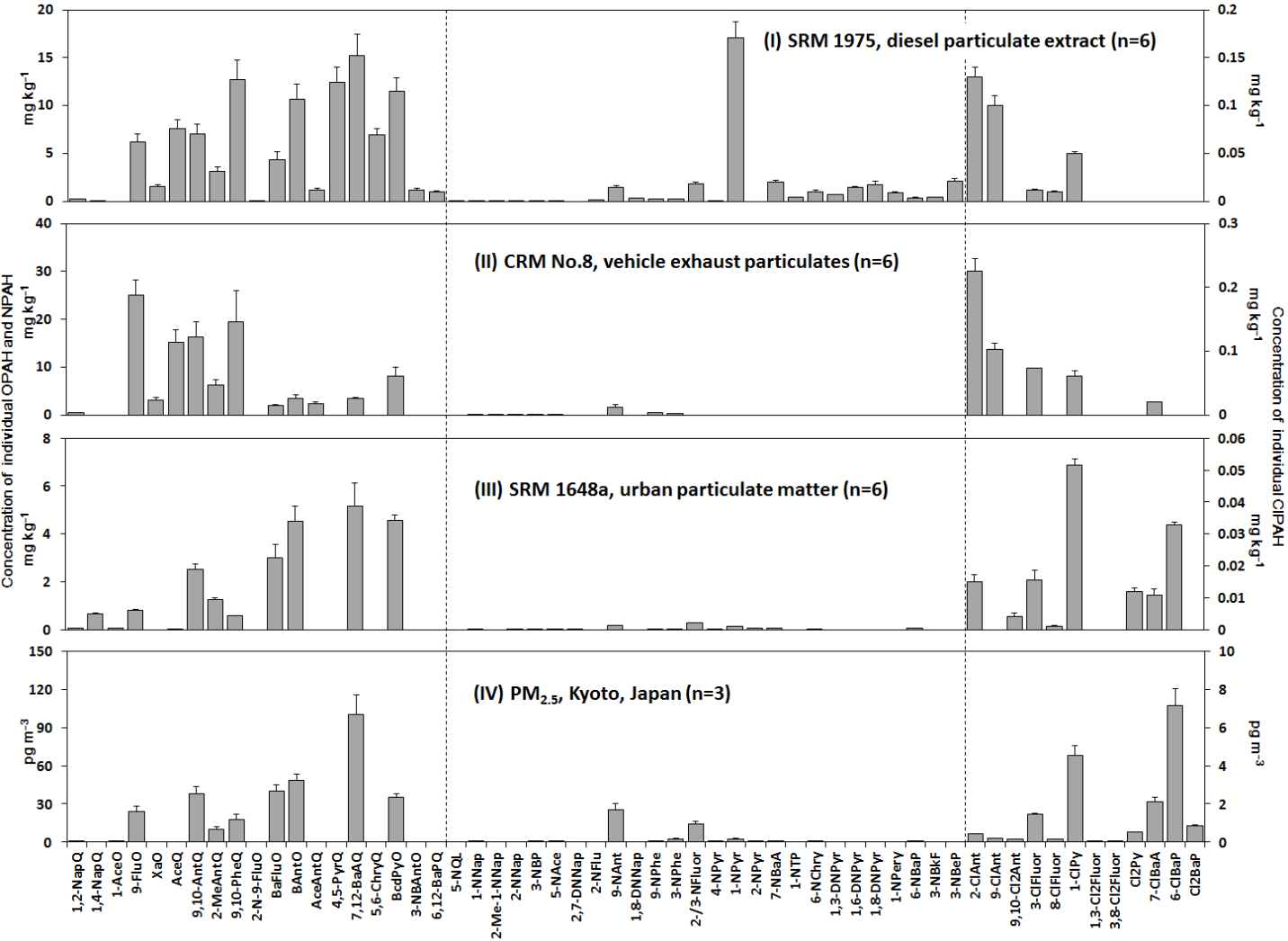
522 Figure 1 Concentrations of PAH derivatives determined by GC-NCI-MS in (I) SRM  
523 1975 (diesel particle extract), (II) CRM No.8 (vehicle exhaust particulate), (III)  
524 SRM 1648a (urban particulate matter), and (IV) PM<sub>2.5</sub> sample from Kyoto,  
525 Japan.

526

527 Figure 2 Comparison of the concentrations obtained using the internal standard ( $n = 6$ )  
528 and standard addition ( $n = 3$ ) quantitation methods. Significantly different at  $p$   
529  $< 0.05$  between IS method vs SA method by Student's  $t$ -test.

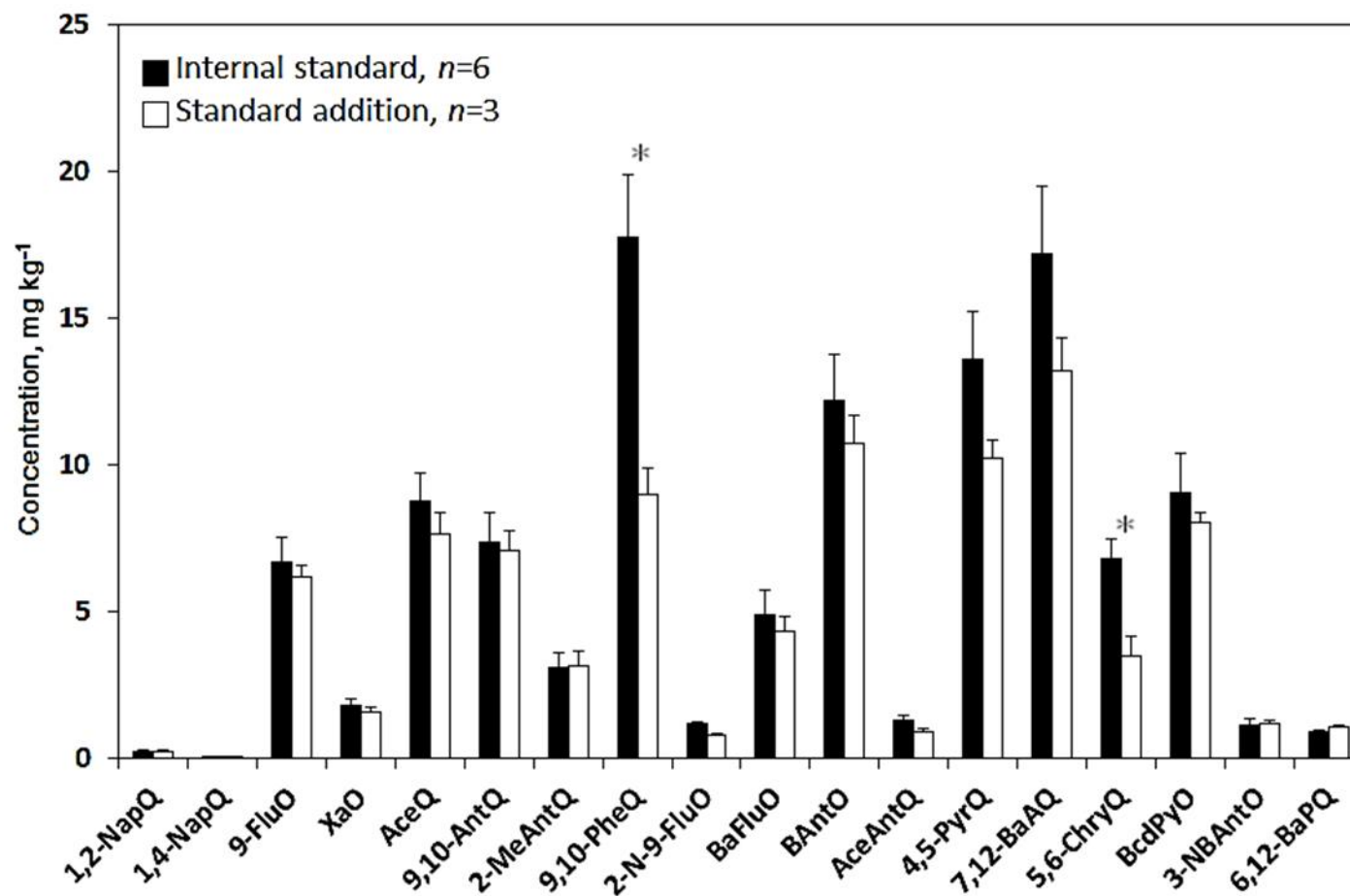
530

531    Figure 1





533 Figure 2



## Supporting Information

Determination of Particle-associated PAH Derivatives (CIPAHs, NPAHs, OPAHs) in  
Ambient Air and Automobile Exhaust by Gas Chromatography/Mass Spectrometry with  
Negative Chemical Ionization

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18 Table S1 GC–MS conditions used to determine PAH derivatives and chromatogram  
19 peak identified number.

No.	Target compound	Abbreviation	<sup>a</sup> RT	Monitored ion (m/z)		b <sub>r</sub> <sup>2</sup>	LOD, pg	<sup>c</sup> Recovery, %		Manufacturer
								QFF	CRM No.8	
OPAHs										
1	1,2-Naphthoquinone	1,2-NapQ	7.96	158	159	0.9984	0.58	75.4	70.1	<sup>d</sup> Sigma-Aldrich
2	1,4-Naphthoquinone	1,4-NapQ	9.44	158	159	0.9958	22.24	71.2	77.2	<sup>e</sup> TCI
5	1-Acenaphthenone	1-AceO	9.67	168	169	0.9934	19.04	84.7	95.6	TCI
9	9-Fluorenone	9-FluO	10.48	180	181	0.9997	0.10	97.8	110.0	Sigma-Aldrich
10	Xanthone	XaO	10.92	196	197	0.9838	90.85	80.1	95.2	Sigma-Aldrich
12	Acenaphthenequinone	AceQ	11.23	182	183	0.9985	9.83	90.7	100.7	Sigma-Aldrich
15	9,10-Anthraquinone	9,10-AntQ	11.86	208	209	0.9990	0.58	96.7	98.5	TCI
16	1,4-Anthraquinone	1,4-AntQ	11.97	208	209	0.9986	46.12	101.5	105.0	TCI
22	2-Methylanthraquinone	2-MeAntQ	12.71	222	223	0.9987	0.63	108.4	100.0	TCI
26	9,10-Phenanthrenequinone	9,10-PheQ	13.23	208	209	0.9996	49.45	108.2	112.2	Sigma-Aldrich
27	2-Nitro-9-fluorenone	2-N-9-FluO	13.39	225	226	0.9967	5.51	95.4	99.3	TCI
36	Benzo[a]fluorenone	BaFluO	14.64	230	231	0.9987	0.50	106.7	110.2	Sigma-Aldrich
39	Benzanthrone	BAntO	15.97	230	231	0.9965	3.87	101.2	113.0	TCI
40	Aceanthrenequinone	AceAntQ	16.24	232	233	0.9957	9.64	85.4	95.8	Sigma-Aldrich
41	4,5-Pyrenequinone	4,5-PyrQ	16.35	232	233	0.9839	60.65	90.4	80.1	Sigma-Aldrich
47	1,6-Pyrenequinone	1,6-PyrQ	16.73	232	233	0.9587	16.11	95.6	92.9	<sup>f</sup> Kanto
48	7,12-Benz[a]anthracenequinone	7,12-BaAQ	16.84	258	259	0.9963	0.44	97.9	99.5	TCI
49	1,8-Pyrenequinone	1,8-PyrQ	16.90	232	233	0.9523	16.95	74.8	101.2	Kanto
52	1,4-Chrysenequinone	1,4-ChryQ	17.50	258	259	0.9685	25.35	87.0	78.5	<sup>g</sup> Chiron
53	2,7-Dinitro-9-fluorenone	2,7-DN-9-FluO	17.58	270	271	0.9987	5.76	88.9	100.2	<sup>h</sup> Accustandard
56	5,12-Naphthacenequinone	5,12-NapthQ	18.97	258	259	0.9908	95.64	87.0	91.3	Sigma-Aldrich
58	5,6-Chrysenequinone	5,6-ChryQ	19.08	258	259	0.9345	91.99	90.1	92.3	<sup>i</sup> MRI
60	6H-Benzo[cd]pyren-6-one	BcdPyO	19.64	254	255	0.9980	3.13	104.7	104.0	Sigma-Aldrich
62	3-Nitrobenzanthrone	3-NBAntO	20.02	275	276	0.9987	2.41	106.5	99.0	Chiron
68	7,10-Benzo[a]pyrenequinone	7,10-BaPQ	21.91	282	283	0.9892	15.37	70.2	110.9	MRI
70	6,12-Benzo[a]pyrenequinone	6,12-BaPQ	23.38	282	283	0.9457	10.96	82.5	100.3	MRI
73	1,6-Benzo[a]pyrenequinone	1,6-BaPQ	24.22	282	283	0.9523	12.39	88.9	95.8	MRI
80	6,13-Pentacenequinone	6,13-PentQ	26.25	308	309	0.9672	21.18	90.0	100.1	TCI
NPAHs										
3	5-Nitroquinoline	5-NQL	9.44	174	175	0.9986	3.87	68.2	77.1	Sigma-Aldrich
4	1-Nitronaphthalene	1-NNap	9.56	173	174	0.9990	0.95	72.8	80.9	TCI
6	2-Methyl-1-nitronaphthalene	2-Me-1-NNap	9.71	187	188	0.9982	7.23	85.7	88.1	TCI
7	2-Nitronaphthalene	2-NNap	9.87	173	174	0.9957	1.64	76.5	90.0	Sigma-Aldrich
8	2-Nitrobiphenyl	2-NBP	10.12	199	200	0.9981	4.12	77.0	70.5	Kanto
11	3-Nitrobiphenyl	3-NBP	10.93	199	200	0.9931	1.46	85.4	82.2	TCI
13	1,5-Dinitronaphthalene	1,5-DNNap	11.58	218	219	0.9957	0.78	88.0	82.0	Sigma-Aldrich
14	1,3-Dinitronaphthalene	1,3-DNNap	11.78	218	219	0.9958	3.91	90.3	90.5	Accustandard
17	5-Nitroacenaphthene	5-NAce	12.07	199	200	0.9578	1.09	94.5	99.9	TCI
20	2,7-Dinitronaphthalene	2,7-DNNap	12.60	218	219	0.9782	8.33	72.9	88.2	Sigma-Aldrich
21	2-Fluoro-7-nitrofluorene	2-F-7-NFlu	12.70	229	230	0.9632	4.25	80.6	101.8	Sigma-Aldrich
23	2-Nitrofluorene	2-NFlu	12.73	211	212	0.9987	2.95	104.0	115.2	Chiron
24	9-Nitroanthracene	9-NAnt	12.92	223	224	0.9991	0.10	94.7	101.0	Sigma-Aldrich
25	1,8-Dinitronaphthalene	1,8-DNNap	13.01	218	219	0.9963	3.84	99.0	105.6	Accustandard
29	9-Nitrophenanthrene	9-NPhe	13.46	223	224	0.9951	4.83	99.2	98.6	Accustandard
30	3-Nitrophenanthrene	3-NPhe	13.83	223	224	0.9985	7.74	98.5	107.5	Accustandard
34	2-Nitroanthracene	2-NAnt	14.23	223	224	0.9852	10.45	99.4	110.2	Accustandard
35	9,10-Dinitroanthracene	9,10-DNAnt	14.31	268	269	0.9657	10.85	99.0	90.5	Accustandard
42	2-Nitrofluoranthene	2-NFluor	16.37	247	248	0.9987	3.13	107.1	98.7	Chiron
43	3-Nitrofluoranthene	3-NFluor	16.40	247	248	0.9988	2.27	106.0	96.0	<sup>j</sup> Wako
45	4-Nitropyrene	4-NPyr	16.57	247	248	0.9756	5.68	105.0	90.1	TCI
50	1-Nitropyrene	1-NPyr	16.98	247	248	0.9968	1.68	104.2	99.0	TCI
51	2-Nitropyrene	2-NPyr	17.20	247	248	0.9985	17.54	98.0	105.8	Chiron
57	7-Nitrobenz[a]anthracene	7-NBaA	18.98	273	274	0.9961	11.08	112.1	100.2	Accustandard
59	1-Nitrotriphenylene	1-NTP	19.08	273	274	0.9981	15.07	115.2	110.3	HPC
61	6-Nitrochrysene	6-NChry	19.95	273	274	0.9930	10.61	102.5	99.6	Chiron
64	2-Nitrotriphenylene	2-NTP	20.72	273	274	0.9970	22.82	106.2	98.0	Chiron
65	1,3-Dinitropyrene	1,3-DNPyr	20.76	292	293	0.9961	7.04	100.4	90.0	Accustandard
66	1,6-Dinitropyrene	1,6-DNPyr	21.43	292	293	0.9960	14.40	95.4	88.5	Accustandard
67	1,8-Dinitropyrene	1,8-DNPvr	21.88	292	293	0.9963	12.97	99.5	96.3	Accustandard

71	1-Nitroperylene	1-NPery	23.44	297	298	0.9987	16.93	121.8	102.2	Chiron
72	6-Nitrobenzo[a]pyrene	6-NBaP	23.58	297	298	0.9996	11.07	103.5	112.0	Accustandard
74	3-Nitrobenzo[k]fluoranthene	3-NBkF	24.59	297	298	0.9951	25.49	104.7	108.3	MRI
76	3-Nitrobenzo[e]pyrene	3-NBeP	25.00	297	298	0.9957	10.21	100.2	95.6	MRI
77	1-Nitrobenzo[a]pyrene	1-NBaP	25.34	297	298	0.9963	22.41	110.0	105.3	MRI
78	3-Nitrobenzo[a]pyrene	3-NBaP	25.48	297	298	0.9985	21.03	101.2	110.9	MRI
79	3-Nitroperylene	3-NPery	25.72	297	298	0.9987	29.50	112.3	118.2	Chiron
<i>C1PAHs</i>										
18	2-Chloroanthracene	2-ClAnt	12.07	212	214	0.9996	7.02	86.4	90.2	Sigma-Aldrich
19	9-Chloroanthracene	9-ClAnt	12.10	212	214	0.9878	7.54	74.0	88.0	Sigma-Aldrich
28	9,10-Dichloroanthracene	9,10-Cl <sub>2</sub> Ant	13.43	246	248	0.9943	1.45	77.0	95.3	<sup>k</sup> Dr. Ohura
31	3-Chlorofluoranthene	3-ClFluor	14.03	236	238	0.9978	0.58	97.0	88.7	Dr. Ohura
32	8-Chlorofluoranthene	8-ClFluor	14.08	236	238	0.9994	0.77	95.3	99.0	Dr. Ohura
33	1-Chloropyrene	1-ClPyr	14.11	236	238	0.9924	2.74	101.2	92.0	Dr. Ohura
37	1,3-Dichlorofluoranthene	1,3-Cl <sub>2</sub> Fluor	15.45	270	272	0.9996	0.09	110.2	98.3	Dr. Ohura
38	3,8-Dichlorofluoranthene	3,8-Cl <sub>2</sub> Fluor	15.95	270	272	0.9998	0.08	98.3	99.0	Dr. Ohura
44	Dichloropyrene	Cl <sub>2</sub> Pyr	16.51	270	272	0.9997	1.02	105.2	99.1	Dr. Ohura
46	3,4-Dichlorofluoranthene	3,4-Cl <sub>2</sub> Fluor	16.58	270	272	0.9996	0.12	104.0	110.3	Dr. Ohura
54	7-Chlorobenz[a]anthracene	7-ClBaA	17.83	262	264	0.9674	1.07	96.9	89.0	Dr. Ohura
55	Trichloropyrene	Cl <sub>3</sub> Pyr	18.33	304	306	0.9968	1.57	99.1	92.6	Dr. Ohura
63	Tetrachloropyrene	Cl <sub>4</sub> Pyr	20.14	340	338	0.9987	1.85	101.1	91.3	Dr. Ohura
69	6-Chlorobenzo[a]pyrene	6-ClBaP	22.37	286	288	0.9875	0.74	96.3	100.0	Dr. Ohura
75	Dichlorobenzo[a]pyrene	Cl <sub>2</sub> BaP	24.92	320	322	0.9984	0.94	90.1	112.2	Dr. Ohura
81	Trichlorobenzo[a]pyrene	Cl <sub>3</sub> BaP	27.24	354	356	0.9965	0.87	95.2	98.9	Dr. Ohura

<sup>a</sup>Retention time

<sup>b</sup>Correlation coefficient

<sup>c</sup>Recovery experiment (%) of each sample; QFF (*n*=3) or CRM No.8 (*n*=3).

<sup>d</sup>Sigma-Aldrich (MO, USA)

<sup>e</sup>Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan)

<sup>f</sup>Kanto Chemical Co., Inc. (Tokyo, Japan)

<sup>g</sup>Chiron AS (Trondheim, Norway)

<sup>h</sup>Accustandard Inc. (CT, USA)

<sup>j</sup>Wako Pure Chemical Industries, Ltd. (Osaka, Japan)

<sup>k</sup>Ohura laboratory (Meijo University, Japan)

22 Figure S1 GC-NCI-MS total ion chromatogram obtained from a standard solution of 28 OPAHs, 37 NPAHs, and 16 CIPAHS (300 pg  $\mu\text{L}^{-1}$ , 1  $\mu\text{L}$   
23 injected, SIM mode). For compounds and peak number identification, refer to Table S1.

